2019

CHEMISTRY

(Major)

Paper : 6.2

(Physical Chemistry)

Full Marks : 60

Time : 3 hours

The figures in the margin indicate full marks for the questions

1. Answer the following in brief : 1×7=7

(a) If three elements *A*, *B* and *C* crystallizes in a cubic solid with *A* atoms at the corners, *B* atoms at the cube centre and *C* atoms at the faces of the cube, what will be the formula of the compound?

(b) Calculate the Miller indices of a crystal plane which cuts through the crystal axes at (6*a*, 3*b*, 3*c*).

(c) "When an intense converging beam of light is passed through a colloidal solution kept in dark, the path of the beam gets illuminated with a bluish light." What is the name of this phenomenon?

(d) Arrange the following in increasing order of their effectiveness in coagulating AS_2S_3 sol :

$$Mg^{2+},\ Na^{+},\ Al^{3+}$$

(e) What do you mean by polydispersity index of a polymer?

(f) Using the Stirling's approximation, calculate $\ln N_A!$. (N_A is Avogadro's number.)

(g) State whether the following statement is True or False :

"In any ionic solid [*MX*] with Schottky defects, the number of positive and negative ions are same."

2. Answer the following questions : 2×4=8

(a) Silver has a cubic unit cell with a cell edge of 408 pm. Its density is $10{\cdot}6\ g\ cm^{-3}$. How many atoms of silver are there in the unit cell?

(b) Distinguish between error and uncertainty in measurement.

(c) The translational partition function for hydrogen atom at 3000 K confined in a vessel of volume $2{\cdot}494\times10^{5}\ cm^{3}$ is $7{\cdot}586\times10^{30}$. Calculate the thermal de Broglie wavelength.

(d) "$CH_3(CH_2)_{15}N(CH_3)_3Br$ forms micelles in aqueous solution at a lower molar concentration than $CH_3(CH_2)_{11}N(CH_3)_3Br$." Explain this observation.

3. (a) What is a semiconductor? Describe the two main types of semiconductors and contrast their conduction mechanisms. What type of semiconductors are the following? 4+1=5

(i) Ge dopped with In

(ii) B dopped with Si

Or

What do you mean by non-stoichiometric defects? Give one example. Explain metal excess and metal deficiency defects with examples. 1+2+2=5

(b) Deduce the relation $S = k\ln W$. 5

Or

Deduce an expression for the entropy of monatomic perfect gas in terms of partition function.

(c) Define average deviation and standard deviation. Estimation of Fe present in a sample showed the following results in a series of experiments :

Experiment	*Amount of Fe*
I	7·146%
II	7·098%
III	6·942%
IV	7·256%
V	6·593%

Find average deviation, standard deviation and coefficient of variations for the values. 2+3=5

4. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) What do you mean by packing efficiency? Calculate the packing efficiency of face-centred cubic arrangement. 1+2=3

(b) KNO_3 crystallizes in orthorhombic system with the unit cell dimensions a=542 pm, b=917 pm and c=645 pm. Calculate the diffraction angle for first-order X-ray reflections from (1 0 0), (0 1 0) and (1 1 1) planes using radiation with wavelength 154·1 pm. 4

(c) White coloured zinc oxide turns yellow on heating. Explain. 3

(d) State Bragg's law and deduce the equation $2d\sin\theta = n\lambda$, symbols have their usual meanings. 4

(e) Explain the following : 1½×2=3

(i) Frenkel defect is not found in pure alkali metal halides.

(ii) Antiferromagnetic substances have unpaired electrons but their dipole moment is zero.

(f) Explain the origin of low temperature superconductivity in terms of Cooper pair. 3

5. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) Discuss the viscometric method of determination of molar mass of polymers. What is viscosity number? 3+1=4

(b) A solution contains 1:2 ratio of number of particles of two substances with molar masses 5000 g mol^{-1} and 12000 g mol^{-1} respectively. Calculate the number average and weight average molar masses. 3

(c) What do you mean by critical micelle concentration? Show graphically how molar conductance, surface tension and osmotic pressure of solutions of surfactants change at the critical micelle concentration. 3

(d) Discuss the kinetics of addition polymerization. Give an example of a polymer produced by this method. 3+1=4

(e) The osmotic pressure of 1 m^3 of a solution containing 2·5 kg of a polymer is found to be 250 Pa at 298 K. Assuming that the solution does not deviate from ideal behaviour, calculate the molar mass of the polymer. 3

(f) What are protective colloids? Explain how a lyophilic colloid can stabilize a lyophobic colloid with suitable examples. 3

6. Answer *either (a), (b)* and *(c) or (d), (e)* and *(f)* :

(a) From the statistical thermodynamical consideration, deduce an expression for the equilibrium constant of an ideal gas reaction equilibrium. 4

(b) If the thermal wavelength of gaseous argon at 25 °C is 16 pm, calculate its standard molar entropy at the same temperature. (Mass of Ar is 39·95 u.) 3

(c) For a diatomic molecule rotating as a rigid rotor, obtain an expression for rotational partition function. 3

(d) Consider the molecule of a gas which have two quantum states of energies 0 and ε and degeneracies g_1 and g_2 respectively. Calculate the contribution of these quantum states to the molar heat capacity of the gas at constant volume. 4

(e) The rotational constant of gaseous HCl, determined from microwave spectroscopy is 10·59 cm^{-1}. Calculate the rotational partition function of HCl at 500 K. 3

(f) Consider a system of six distinguishable particles. One of the macrostate of the system has the following distribution of particles :

Energy level	0	1	2	3	4
Number of particles	1	0	2	1	2

Find the thermodynamic probability. 3

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